off in vacuo, the residual oil was dissolved in $CHCl_3$ (6 mL). This solution was added to a mixture of **1** (512 mg, 3 mmol) and $AlCl_3$ (800 mg, 6 mmol) in $CHCl_3$ (9 mL), and this was stirred for 12 h at room temperature. The reaction mixture was poured onto small amounts of ice and neutralized with aqueous Na_2CO_3. Products were extracted with $CHCl_3$, and the combined $CHCl_3$ extract was evaporated to give a solid which was recrystallized from $CHCl_3$ to give **24**. Compounds **26** and **28** were also obtained in this way.[36]

***O*-(1-Adamantyl)propionaldoxime (32).** A mixture of 1 (171 mg, 1 mol), **31** (145 mg, 1 mmol), and $ZnCl_2$ (273 mg, 2 mmol) in $CHCl_3$ (5 mL) was stirred vigorously for 48 h at room temperature. Water was then added to this mixture, and the organic layer was separated and dried (Na_2SO_4). Evaporation of the solvent gave an oil which was purified by chromatography on silica gel (benzene) to give **32**. Compounds **34** and **39** were also obtained in this way.[36]

α-Phenyl-*N*-(1-adamantyl)nitrone (35). To a mixture of 1 (171 mg, 1 mmol) and $AlCl_3$ (133 mg, 1 mmol) in $CHCl_3$ (5 mL) was added **33** (193 mg, 1 mmol) dropwise at −40 °C under a nitrogen atmosphere. Stirring was continued for 100 min while the reaction temperature was gradually raised to 0 °C. The reaction mixture was then poured onto ice–water, and the separated organic layer was washed with water and dried (Na_2SO_4). The solvent was evaporated off to leave the residue which was chromatographed on a silica gel column ($CHCl_3$) to give **35**.[36] An independent synthesis was carried out by condensation of **36** with benzaldehyde as follows. Free **36**[37] liberated from its HCl salt (30 mg, 0.15 mmol) with triethylamine in benzene was refluxed with benzaldehyde (21 mg, 0.2 mmol) and a trace of acetic acid in ethanol (2 mL) for 2 h. After removal of the solvent, the residue was chromatographed on a silica gel column ($CHCl_3$) to give **35** (30 mg, 82%). The spectral comparison of this authentic sample with the product obtained as above affirmed the assigned structure. A solution of **35** (100 mg, 0.39 mmol) and diethyl acetylenedicarboxylate (68 mg, 0.4 mmol) in benzene (5 mL) was refluxed for 90 min. After removal of the solvent, the residue was chromatographed on an alumina column (ethyl acetate/benzene, 2:1) to give a 1:1 adduct (**37**): 100 mg (66%); mp 95–96 °C; IR (KBr) 1745, 1695, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.5 (m, 5 H, phenyl), 5.53 (s, 1 H, C_3 H), 4.36 and 4.04 (dq, J = 7.0 Hz, OCH_2), 1.5–2.3 (m, 15 H, adamantane), 1.37 and 1.12 (dt, 6 H, J = 7.0 Hz, CH_3). Anal. Calcd for $C_{25}H_{31}NO_5$: C, 70.57; H, 7.34; N, 3.29. Found: C, 70.86; H, 7.43; N, 3.41.

α-Chloro-β-(1-adamantyl)styrene (41). A mixture of 1 (307 mg, 1.8 mmol), **40** (348 mg, 2 mmol), and $ZnCl_2$ (800 mg, 5.9 mmol; commercial product) in CH_2Cl_2 (4 mL) was stirred for 48 h at room temperature. After filtration of the catalyst and removal of the solvent, the residual oil was chromatographed on a silica gel column (*n*-hexane) to give **41**. Acetylene **44** was obtained under the same conditions except for the use of purified $ZnCl_2$ (recrystallized from dioxane).[36]

Wittig Reaction of 42. To an ethereal solution of benzylidenetriphenylphosphorane[38] prepared from the corresponding phosphonium bromide (650 mg, 1.5 mmol) and phenyllithium (1.5 mmol) was added **42** (164 mg, 1 mmol) in dry ether under a nitrogen atmosphere, and this mixture was stirred overnight at room temperature. After decomposition with water, the ether layer was separated and dried (Na_2SO_4). The solvent was evaporated off, and the residual oil was subjected to silica gel chromatography (*n*-hexane). The first fraction was identified as *cis*-β-(1-adamantyl)styrene: oil; 70 mg (29%); IR (film) 1630, 1600, 1490, 710 cm^{-1}; ^1H NMR (CCl_4) δ 7.08 (s, 5 H, phenyl), 6.30 and 5.23 (AB q, each 1 H, J = 12.7 Hz, HC=CH), 1.5–2.0 (m, 15 H, adamantane). The second fraction was identified as the trans isomer: crystalline; 30 mg (13%); mp 72–74 °C; IR (KBr) 1630, 1600, 1490, 960 cm^{-1}; ^1H NMR (CCl_4) δ 7.15 (s, 5 H, phenyl), 6.22 and 5.90 (AB q, each 1 H, J = 16.5 Hz, HC=CH), 1.6–2.2 (m, 15 H, adamantane). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found (cis): C, 90.75; H, 9.25. Found (trans): C, 90.98; H, 9.02.

The cis isomer was consistent with the reduced product of the reaction of **41** (40 mg) with zinc metal (100 mg) in refluxing ethanol (2 mL) for 16 h.

***p*-(1-Adamantyl)phenol (56).** A mixture of 1-adamantyl bromide (215 mg, 1 mmol) and **55** (332 mg, 2 mmol) was heated for 5 h at 140 °C. After the mixture cooled, the resulting solid was recrystallized from ether to give **56**.[36]

Registry No. 1, 935-56-8; **5**, 762-72-1; **6**, 22922-62-9; **7**, 19752-23-9; **8**, 74203-25-1; **9**, 13361-64-3; **10**, 74203-26-2; **11**, 770-09-2; **12**, 70624-77-0; **13**, 6651-34-9; **14**, 74203-27-3; **14**-DNP, 74203-28-4; **15**, 6651-36-1; **16**, 41031-34-9; **17**, 7449-74-3; **18**, 3717-37-1; **19**, 74203-29-5; **20**, 74203-30-8; **21**, 149-30-4; **22**, 74203-31-9; **23**, 66-22-8; **24**, 74203-32-0; **25**, 591-28-6; **26**, 74203-33-1; **27**, 51-21-8; **28**, 74203-34-2; **29**, 18292-04-1; **30**, 70624-78-1; **31**, 18140-10-8; **32**, 74203-35-3; **33**, 17876-73-2; **34**, 19026-84-7; **35**, 31463-28-2; **38**, 74203-36-4; **39**, 74203-37-5; **40**, 2170-06-1; **41**, 74203-38-6; **42**, 2094-74-8; *trans*-**43**, 70624-80-5; *cis*-**43**, 70624-81-6; **44**, 74203-39-7; **45**, 19372-00-0; **46**, 18156-74-6; **47**, 26845-71-6; **48**, 13435-08-0; **49**, 74203-40-0; **50**, 32137-73-8; **51**, 74203-41-1; **52**, 7450-03-5; **53**, 1459-55-8; **54**, 3728-44-7; **55**, 15288-53-6; **56**, 29799-07-3; benzaldehyde, 100-52-7; diethyl acetylenedicarboxylate, 762-21-0; benzylidenetriphenylphosphorane, 16721-45-2; 1-adamantyl bromide, 768-90-1.

(37) G. Zinner and U. Dybowski, *Arch. Pharm. (Weinheim, Ger.)*, **303**, 488 (1970).

(38) G. Wittig and U. Schoellkopf, *Chem. Ber.*, **87**, 1318 (1954).

Syntheses and Properties of Dimethylbisdehydro[15]annulenone, -[17]annulenone, -[19]annulenone, and -[21]annulenone

Jûro Ojima,*[1] Yûji Shiroishi,[1a] Kazuyo Wada,[1a] and Franz Sondheimer[1b]

Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930, Japan, and Chemistry Department, University College, London WCIH OAJ, England

Received March 17, 1980

Syntheses of 5,10-dimethyl-6,8-bisdehydro[15]annulenone (**2**), 7,12-dimethyl-8,10-bisdehydro[17]annulenone (**3**), 7,12-dimethyl-8,10-bisdehydro[19]annulenone (**4**), and 9,14-dimethyl-10,12-bisdehydro[21]annulenone (**5**) are described. The ^1H NMR spectra of these annulenones indicate that both **2** and **4** are diatropic, whereas both **3** and **5** are paratropic, and these ring currents are increased by dissolution in deuteriotrifluoroacetic acid.

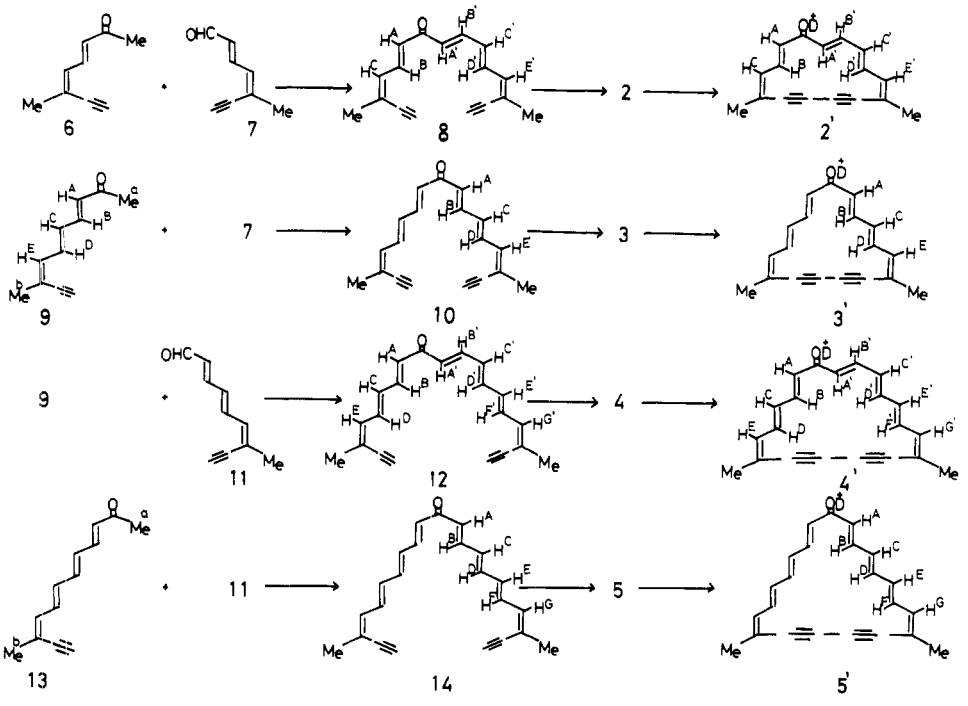
Syntheses of a series of bis(cyclohexene)-annelated bisdehydro[13]-, -[15]-, and -[17]annulenones have been described previously.[2] Since this work was carried out, it has been shown that monocyclic bisdehydroannulenes with methyl substituents on the propargylic positions are superior to the corresponding cyclohexene-fused compounds for the investigation of conformational mobility

(1) (a) Toyama University. (b) University College. Part of this work was carried out by J. Ojima at University College on leave from Toyama University.

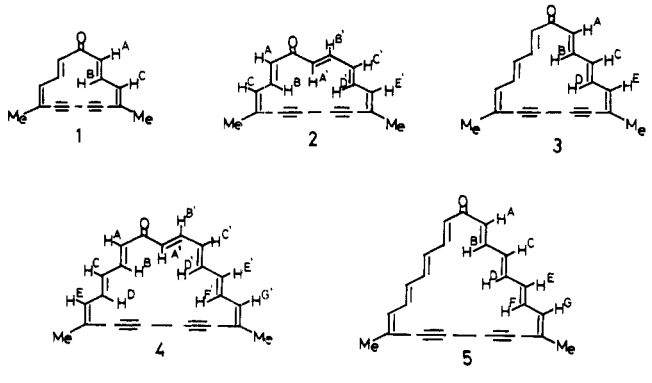
(2) P. D. Howes, E. LeGoff, and F. Sondheimer, *Tetrahedron Lett.*, 3691, 3695 (1972).

0022-3263/80/1945-3564$01.00/0

Scheme I



and ring current effects.[3] It was therefore decided to prepare a series of dimethylbisdehydroannulenones, the simplest one of which, the dimethylbisdehydro[13]-annulenone (1), has already been reported.[4] In the present paper, we describe in full syntheses of higher vinylogues of 1, namely, the dimethylbisdehydro[15]annulenone 2,[5a] -[17]annulenone 3,[5b] -[19]annulenone 4,[5c] and -[21]-annulenone 5[5d] (part of the present work has appeared in



preliminary reports,[6] and some properties of 2–4 have been quoted previously[7]). Compounds 1–5 are members of a series of monocyclic dehydroannulenones in which the number of double bonds is increased systematically, and a study of their spectral properties (both in neutral solvents and in trifluoroacetic acid) was particularly informative. It may be mentioned that the bisdehydo[19]annulenone 4 and -[21]annulenone 5 are the largest ring monocyclic annulenone derivatives to be obtained.[8]

Compounds 2–5 were synthesized essentially by the same procedures as used for 1,[4] employing an aldol condensation of an appropriate aldehyde and ketone containing terminal acetylenes, followed by intramolecular oxidative coupling of the resulting terminal diacetylene. For this purpose, vinylogues of (*Z*)-3-methyl-2-penten-4-yn-1-al[4] and 6-methyl-3,5-octadien-7-yn-2-one (6)[4,9] (the starting materials for the synthesis of 1) were required. The homologation of (*Z*)-3-methyl-2-penten-4-yn-1-al to (2*E*,4*Z*)-5-methyl-2,4-heptadien-6-yn-1-al (7), using Isler's method[10] or Wittig condensation,[11] has already been reported,[7c] as well as the further homologation of 7 to (2*E*,4*E*,6*Z*)-7-methyl-2,4,6-nonatrien-8-yn-1-al (11).[12]

Aldol condensation of 6 and 7 in ether with methanolic potassium hydroxide gave 42% 3,13-dimethyl-3,5,8,10,12-pentadecapentaene-1,14-diyn-7-one (8) (Scheme I). The structure and stereochemistry of 8 were determined by the ^{1}H NMR spectrum determined in the presence of Eu(fod)$_3$ shift reagent. Oxidative coupling of 8 with cupric acetate monohydrate in pyridine at 60 °C led to 16% dimethylbisdehydro[15]annulenone 2 as yellow needles, mp 162–163 °C dec. Subsequently, it was found that oxidative couplings of this type proceed in higher yield when anhydrous cupric acetate in pyridine–ether at 50 °C is employed,[4,13]

(3) See (a) R. L. Wife and F. Sondheimer, *J. Am. Chem. Soc.*, **97**, 640 (1975); (b) *Tetrahedron Lett.*, 195 (1975).

(4) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, **42**, 2130 (1977).

(5) IUPAC nomenclature: (a) 5,10-dimethyl-2,4,10,12,14-cyclopentadecapentaene-6,8-diyn-1-one; (b) 7,12-dimethyl-2,4,6,12,14,16-cycloheptadecahexaene-8,10-diyn-1-one; (c) 7,12-dimethyl-2,4,6,12,14,16,18-cyclononadecaheptaene-8,10-diyn-1-one; (d) 9,14-dimethyl-2,4,6,8,14,16,18,20-cycloheneicosaoctaene-10,12-diyn-1-one.

(6) (a) See J. Ojima and F. Sondheimer, Abstracts of papers, 30th Annual Meeting of the Chemical Society of Japan, Osaka, Apr 1974. (b) See J. Ojima et al., Abstracts of Papers, 11th Symposium on Nonbenzenoid Aromatic Compounds of the Chemical Society of Japan, Osaka, Oct 1978.

(7) (a) R. L. Wife, P. J. Beeby, and F. Sondheimer, *J. Am. Chem. Soc.*, **97**, 641 (1975), and ref 3; (b) J. Ojima, Y. Yokoyama, and M. Enkaku, *Bull. Chem. Soc. Jpn.*, **50**, 1522 (1977); (c) J. Ojima, M. Ishiyama, and A. Kimura, *ibid.*, **50**, 1584 (1977); (d) J. Ojima, K. Kanazawa, K. Kusaki, and K. Wada, *Chem. Lett.*, 1009 (1978); *J. Chem. Soc., Perkin Trans. 1*, 473 (1980); (e) J. Ojima, K. Wada, and K. Kanazawa, *Chem. Lett.*, 1035 (1979); (f) J. Ojima, K. Wada, Y. Nakagawa, M. Terasaki, and Y. Jūni, *ibid.*, 225 (1980).

(8) For a review of annulenones, see T. M. Cresp and M. V. Sargent, *Top. Curr. Chem.*, **No. 57**, 111 (1975).

(9) J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **49**, 292 (1976).

(10) O. Isler, H. Linder, M. Montavon, H. Rüegg, and P. Zeller, *Helv. Chim. Acta.*, **39**, 240 (1956); H. Rüegg, H. Montavon, G. Saucy, H. Schwieter, and O. Isler, *ibid.*, **42**, 854 (1959).

(11) T. M. Cresp, M. V. Sargent, and P. Vogel, *J. Chem. Soc., Perkin Trans. 1*, 37 (1974); J. Ojima, A. Kimura, Y. Yokoyama, and T. Yokoyama, *Bull. Chem. Soc. Jpn.*, **48**, 367 (1975).

(12) J. Ojima, Y. Shiroishi, and M. Fujiyoshi, *Bull. Chem. Soc. Jpn.*, **51**, 2112 (1978).

Table I. Electronic Absorption Maxima of Dimethylbisdehydro[13]- (1), -[15]- (2), -[17]- (3), -[19]- (4), and -[21]annulenones (5) in Tetrahydrofuran [λ_{max} (ϵ_{max})]

1[a]	2	3	4	5
~250 (sh, 25 800)	246 (13 100)	265 (17 300)	248 (15 900)	245 (14 800)
262 (37 900)	258 (14 300)	282 (31 900)	254 (16 800)	255 (sh, 14 000)
273 (39 900)	305 (35 900)	297 (45 400)	260 (17 100)	307 (sh, 52 200)
387 (990)	385 (7190)	306 (46 600)	278 (17 900)	327 (84 200)
		403 (sh, 3650)	329 (51 300)	340 (92 300)
			420 (sh, 6150)	415 (sh, 7110)

[a] In ether, see ref 4.

Table II. Electronic Absorption Maxima of Dimethylbisdehydro[13]- (1), -[15]- (2), -[17]- (3), -[19]- (4), and -[21]annulenones (5) in Trifluoroacetic Acid [λ_{max} (Relative Extinction Coefficients)][a]

1[b]	2	3	4	5
~269 (sh, 0.82)	292 (0.08)	331 (1.00)	295 (sh, 0.43)	271 (0.67)
281 (1.00)	352 (sh, 0.68)	343 (sh, 0.92)	302 (0.50)	308 (0.61)
~350 (sh, 0.12)	367 (1.00)	380 (0.21)	362 (sh, 0.55)	374 (1.00)
	496 (sh, 0.15)		410 (1.00)	425 (0.54)
	513 (0.19)		425 (0.96)	450 (sh, 0.39)
	555 (0.34)		565 (sh, 0.25)	486 (sh, 0.29)
			618 (0.34)	660 (0.20)
			664 (0.31)	

[a] All the spectra showed tailing to ~700 nm. [b] See ref 4.

and the yield of **2** from **8** could be improved to 48% under these conditions. The dehydro[15]annulenone **2** has therefore become a relatively readily available substance, which made it desirable to utilize this compound for the synthesis of a fulvalene derivative.[14]

Aldol condensation of **7** and acetone in the presence of aqueous ethanolic sodium hydroxide led to 8-methyl-3,5,7-decatrien-9-yn-2-one (**9**) in 78% yield. A second condensation of **7** and **9**, as that between **6** and **7**, then gave 41% 3,15-dimethyl-3,5,7,10,12,14-heptadecahexaene-1,16-diyn-9-one (**10**). Oxidative coupling of **10** with cupric acetate monohydrate in pyridine at 60 °C led to 38% dimethylbisdehydro[17]annulenone **3** as red needles, mp 207 °C dec. The yield of **3** from **10** could not be improved when anhydrous cupric acetate in pyridine-ether was used.[4,13]

Similarly, aldol condensation of the trienyne aldehyde **11** and the ketone **9** in the presence of ethanolic sodium ethoxide gave 63% 3,17-dimethyl-3,5,7,10,12,14,16-nonadecaheptaene-1,18-diyn-9-one (**12**). Oxidative coupling of **12** with cupric acetate monohydrate in pyridine at 60 °C yielded none of the desired bisdehydro[19]annulenone **4**. However, use of the improved method (anhydrous cupric acetate in pyridine–ether) led to the dimethylbisdehydro[19]annulenone **4** as orange needles, mp 124–125 °C, in 5.2% yield.

Aldol condensation of the trienyne aldehyde **11** and acetone in the presence of aqueous ethanolic sodium hydroxide led to 54% 10-methyl-3,5,7,9-dodecatetraen-11-yn-2-one (**13**). A second aldol condensation of **11** and **13**, as that between **9** and **11**, then gave 31% 3,9-dimethyl-3,5,7,9,12,14,16,18-heneicosaoctaene-1,20-diyn-11-one (**14**). Oxidation of **14** with anhydrous cupric acetate in pyridine–ether, as before, led to the dimethylbisdehydro-[21]annulenone **5** as red needles, mp 159–160 °C, in 8.1% yield.

Treatment of the annulenones **2–5** with trifluoroacetic acid or deuteriotrifluoroacetic acid gave the corresponding protonated or deuterated carbonyl species **2′–5′**; **2′** was purple, **3′** was dark green, **4′** was dark purple, and **5′** was dark green. Quenching of **2′**, **3′**, and **5′** with aqueous sodium bicarbonate resulted in regeneration of **2**, **3**, and **5**, respectively. Keeping the species **4′** resulted in a change (now under investigation), and the ketone **4** was not recovered from it on quenching.

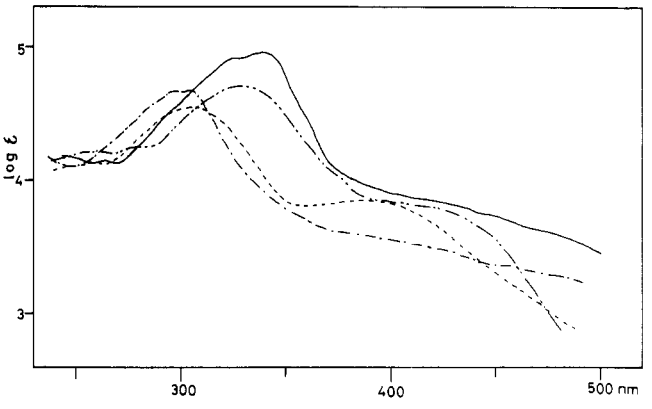


Figure 1. UV spectra of the dimethylbisdehydro[15]- (**2**) (---), -[17]- (**3**) (– – –), -[19]- (**4**) (– – – –), and -[21]annulenone (**5**) (—) in tetrahydrofuran.

The electronic absorption spectra (in tetrahydrofuran) of the dimethylbisdehydroannulenones **2–5** are illustrated in Figure 1, and the absorption maxima of these annulenones as well as the dimethylbisdehydro[13]annulenone **1**[4] are listed in Table I. Although the main maxima of the dimethylbisdehydroannulenones exhibit a bathochromic shift as the ring size increases, this shift is very small between the [15]annulenone **2** and the [17]-annulenone **3** and between the [19]annulenone **4** and the [21]annulenone **5**. In fact, it is apparent from Figure 1 that the electronic spectra of the [$4n$ – 1]annulenones **2** and **4** are rather similar to those of the [$4n$ + 1]annulenones **3** and **5**, respectively. Clearly, this is due to the occurrence of the same sort of alternation between the maxima of [$4n$ – 2) and $4n$ systems, as has been observed for the annulenes and dehydroanulenes [$(4n - 2)\pi$ systems absorbing at higher wavelengths than the $4n$ systems].[15]

(13) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, **42**, 1960 (1977), and ref 12.

(14) See T. Asao et al., Abstracts of Papers, 12th Symposium on Nonbenzenoid Aromatic Compounds of the Chemical Society of Japan, Matsumoto, Sept 1979.

(15) P. J. Garratt and K. Grohmann, *Methoden Org. Chem. (Houben-Weyl)*, **5**, 533 (1972).

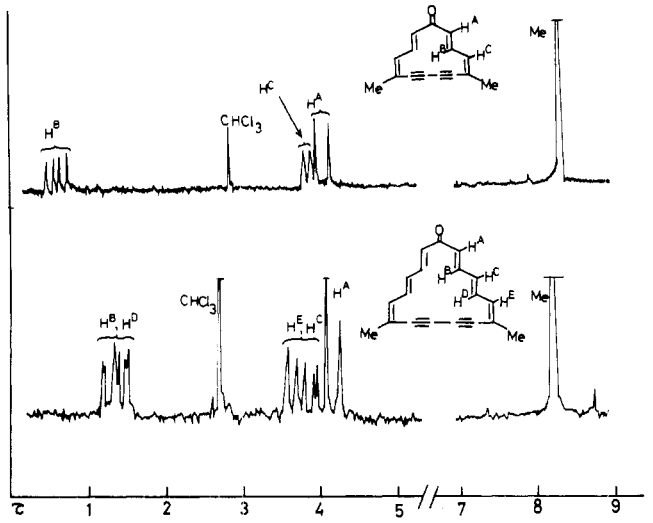
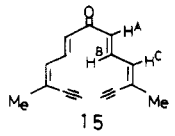


Figure 2. ^{1}H NMR spectra of the dimethylbisdehydro[13]- (**1**) and -[17]annulenone (**3**) in $CDCl_3$ at 35 °C (60 MHz, τ values, internal standard Me_4Si).

The electronic absorption maxima of the annulenones **1–5** in trifluoroacetic acid are given in Table II, and it is evident that protonation with this acid causes the main maxima to shift to higher wavelengths in every case. The bathochromic shifts are much larger in the case of the [4*n* − 1]annulenones **2** and **4** (62–81 nm) than in the case of the [4*n* + 1]annulenones **1**, **3**, and **5** (8–34 nm). Here the alternation is quite clear, the main maxima of the 13-, 15-, 17-, 19-, and 21-membered annulenones in trifluoroacetic acid occurring at 281, 367, 331, 410, and 374 nm, respectively.

The ^{1}H NMR chemical shifts of olefinic and methyl protons of the annulenones **1–5** are listed in Table III, together with those of the corresponding acyclic ketones **15**, **8**, **10**, **12**, and **14**. Individual assignments, some of



15

which are tentative, were made on the basis of multiplicities and coupling constants given in the experimental section.

Comparison of the ^{1}H NMR chemical shifts of the various protons of the bisdehydro[17]annulenone **3** and -[21]annulenone **5** with those of the corresponding acyclic ketones **10** and **14** indicates that both **3** and **5** are paratropic, as might be expected of 16π and 20π systems, respectively, and as has been observed for the 12π-electron system **1**.[4] This follows from the fact that essentially all the outer protons in **3** and **5** (including the methyl protons) resonate at higher field than the corresponding protons in **10** and **14**, respectively, whereas the inner protons in **3** and **5** resonate at lower field. Conversely, comparison of the various protons of **2** and **4** with those of the corresponding acyclic models **8** and **12** indicates that **2** and **4** are diatropic, as might be expected of 14π- and 18π-electron systems, respectively. This follows from the fact that essentially all the inner protons in **2** and **4** resonate at higher field than the corresponding protons in **8** and **12**, respectively, whereas all the outer protons (including the methyl protons) resonate at lower field.

The ^{1}H NMR spectra of the bisdehydroannulenones **1–5** are presented in Figures 2–4. It is evident that in the spectra of **1**, **3**, and **5** (Figures 2 and 4) the outer protons resonate at higher field that the inner protons, while in

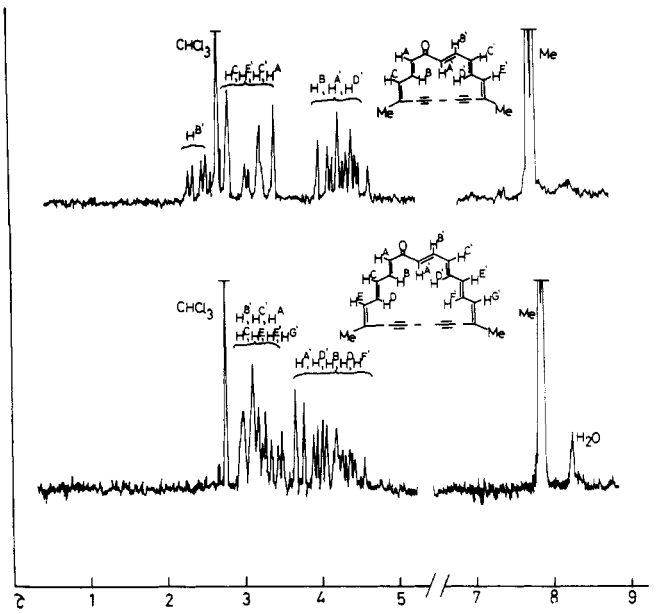


Figure 3. ^{1}H NMR spectra of the dimethylbisdehydro[15]- (**2**) and -[19]annulenone (**4**) in $CDCl_3$ at 35 °C (90 MHz, τ values, internal standard Me_4Si).

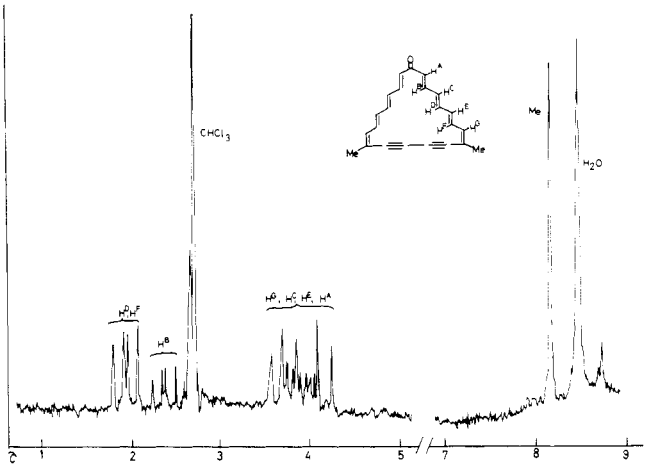


Figure 4. ^{1}H NMR FT spectrum of the dimethylbisdehydro-[21]annulenone (**5**) in $CDCl_3$ at 35 °C (100 MHz, τ values, internal standard Me_4Si).

the spectra of **2** and **4** (Figure 3) the outer protons resonate at lower field than the inner ones. This confirms the indicated conformations for compounds **1–5** and shows that the abovementioned alternation of the ring currents in **1–5** can be deduced without having to make comparisons with the corresponding acyclic models. The simplest test for the nature of the ring currents in **1–5** is provided by the chemical shifts of the methyl protons, since these must always be external and can readily be recognized. The alternation of the methyl proton resonances between the [4*n* + 1]annulenones **1**, **3** and **5** (relatively high field) and the [4*n* − 1]annulenones **2** and **4** (relatively low field) confirms the paratropicity of the former and the diatropicity of the latter.

The ^{1}H NMR chemical shifts of the deuterated species **1′–5′**, obtained by dissolving **1–5** in deuteriotrifluoroacetic acid, are also given in Table III. It is evident that the conformations are unchanged. Comparison of the olefinic proton chemical shifts of **1′–5′** with those of the corresponding acyclic models, as before, indicates that the ring currents of the deuterated species **1′–5′** are much more marked than those of the annulenones **1–5**, respectively. Again, this is seen most simply by inspection of the methyl

Table III. ^{1}H NMR Chemical Shifts of 1–5, 15, 8, 10, 12, 14 (in $CDCl_3$) and 1′–5′ (in CF_3COOD) at 90 MHz, Determined at 35 °C Unless Otherwise Stated (τ Values, Internal Standard, Me_4Si)

compd	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	H^F	$H^{F'}$	H^G	$H^{G'}$	Me
15[a]	3.55		2.32		3.54										7.98
1[a]	3.90		0.61		3.71										8.26
1′[a]	3.85		−0.79		3.88										8.33
Δ(1 − 15)	+0.35		−1.71		+0.17										+0.28
Δ(1′ − 15)	+0.30		−3.11		+0.34										+0.35
8	(3.40–3.72)		2.27	2.60	(3.40–3.72)			2.87		(3.40–3.72)					7.93, 7.97
2	3.35	4.37	4.17	2.44	2.75	3.19		4.53		2.75					7.76, 7.82
2′[b]	1.31	10.10	9.92[g]	0.29[f]	0.89	1.28[f]		10.15[g]		0.89					6.73, 6.82
Δ(2 − 8)			+1.90	−0.16				+1.66							−0.11–−0.21
Δ(2′ − 8)			+7.65	−2.31				+7.28							−1.11–−1.24
10[c]	3.57		2.92		3.61		2.64		3.61						8.01
3[c]	4.20		1.40		3.98		1.37		3.67						8.23
3′[d]	4.29		−1.68[h]		4.36		−1.75[h]		4.09						8.42
Δ(3 − 10)	+0.63		−1.52		+0.37		−1.27		+0.06						+0.22
Δ(3′ − 10)	+0.72		−4.60		+0.75		−4.39		+0.48						+0.41
12	(2.43													3.73)	7.97
4	3.52	3.80	4.10[i]		(2.87-3.22)[k]	3.33[k]	4.15[j]	3.98[i]	(2.87-3.22)			4.35[j]		(2.87-3.22)	7.79, 7.83
4′[e]	(1.2-1.8)	(8.4-9.1)			(1.2	1.8)	(8.4-9.1)		(1.2-1.8)			(8.4-9.1)		(1.2-1.8)	6.96, 7.07
Δ(4 − 12)															−0.14–−0.18
Δ(4′ − 12)															−0.90–−1.01
14[c]	(2.53												3.78)		8.02
5[c]	4.16		2.36		3.88[l]		1.94		3.84[l]		1.94		3.63		8.17
5′[c]	(4.28-4.80)		−1.62		(4.28-4.80)		−2.22[m]		(4.28-4.80)		−2.10[m]		(4.28-4.80)		8.52
Δ(5 − 14)															+0.15
Δ(5′ − 14)															+0.50

[a] At 100 MHz, see ref 4. [b] Determined with CH_2Cl_2 as an internal standard. [c] At 100 MHz. [d] At 60 MHz. [e] At 100 MHz, determined with CH_2Cl_2 as an internal standard. This spectrum changed on standing. [f–m] Assignments may be reversed in each group of the column (see Experimental Section).

proton resonances, the alternation of which in 1′–5′ is considerably greater than in 1–5.

Experimental Section

General Procedures. Melting points were determined on a hot-stage apparatus and are uncorrected. Infrared spectra were measured on a Unicam SP 200 or a Hitachi EPI-S2 spectrophotometer (s = strong, m = medium, w = weak); only significant maxima are reported. Electronic spectra were determined on a Unicam SP 800 or a Hitachi 124 spectrophotometer (sh = shoulder). ^{1}H NMR spectra were measured on a Varian T60 (60 MHz), a Varian EM-390 (90 MHz), a Varian XL-100 (100 MHz) or a JEOL MH-100 (100 MHz) spectrometer, tetramethylsilane being used as an internal standard unless otherwise stated. Assignments were assisted by the addition of Eu(fod)$_3$ shift reagent in some cases. Mass spectra were determined on an AEI MS-12 (70 eV) or a JEOL-MS-OI-SG-2 (75 eV) spectrometer. Alumina for column chromatography refers to Woelm neutral alumina activity III or Merck activity II–III. Compounds were preadsorbed from ether or benzene solution onto alumina before being applied to the column. Organic extracts were washed with saturated aqueous sodium chloride and dried over magnesium sulfate or sodium sulfate immediately prior to solvent removal. Freshly deoxygenated ether was used to minimize oxidation of the compounds employed for aldol condensation and was prepared by passing through a short column of Woelm basic alumina (activity I), followed by flushing with nitrogen, immediately before use.

3,13-Dimethyl-3,5,8,10,12-pentadecapentaene-1,14-diyn-7-one (8). Methanolic potassium hydroxide (3.6 N, 6 mL) was added to a stirred solution of aldehyde 7[7c] (2.60 g, 22 mmol) and ketone 6[4,9] (2.01 g, 15 mmol) in deoxygenated ether (60 mL) at 0 °C. After 1.5 h at 0 °C, acetic acid (6 mL) was added, followed by stirring for 15 min and then dilution with water. The separated aqueous layer was extracted with ether and the combined ethereal extracts were washed with saturated aqueous sodium bicarbonate. The residue after solvent removal was chromatographed on a column of alumina (Woelm, 100 g). Fractions eluted with 20% ether–pentane on evaporation yielded the ketone 8 (1.50 g, 42%), yellow needles, mp 105–106 °C, from hexane–benzene: mass spectrum, m/e 236 (M^+, 50%), 178 (100); mol wt 236.3; UV (Et_2O) λ_{max} 229 (sh, ϵ 6340), 247 (sh, 9420), 255 (sh, 11 200), 273 (12 100), 285 (sh, 11 600), 301 (sh, 12 800), 359 (sh, 31 400); IR (KBr) 3250 (m, C≡CH), 2100 (w, C≡C), 1655 (m, C=O), 1605 (s), 1595 (s, C=C), 1000 cm^{-1} (s, trans HC=CH); ^{1}H NMR (90 MHz, $CDCl_3$) τ 2.27 (dd, J = 15, 11 Hz, 1 H, H^B), 2.60 (dd, J = 15, 11 Hz, 1 H, $H^{B'}$), 2.87 (dd, J = 15, 11 Hz, 1 H, $H^{D'}$), 3.40–3.72 (m, 5 H, H^A, $H^{A'}$, H^C, $H^{C'}$, $H^{E'}$), 6.48 (s, 1 H, C≡CH), 6.55 (s, 1 H, C≡CH), 7.93 (s, 3 H, Me), 7.97 (s, 3 H, Me).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.64; H, 6.62.

5,10-Dimethyl-6,8-bisdehydro[15]annulenone (2). A solution of ketone 8 (355 mg, 1.50 mmol) in pyridine and dry ether (3:1, 34 mL) was added dropwise during 2 h to a stirred solution of anhydrous cupric acetate (1.95 g) in pyridine and dry ether (3:1, 99 mL) at 50–55 °C (bath). The solution was stirred at 53 °C for a further 30 min and was then cooled. After addition of benzene (100 mL), the mixture was filtered through Hyflo Super-Cel.[16] The precipitates were washed with benzene, and the filtrate was poured into water. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic extracts were washed with 3 N hydrochloric acid and aqueous sodium bicarbonate. The dark red liquid obtained after removal of solvent was chromatographed on alumina (Merck, 70 g). Elution with hexane–ether (4:1) afforded the annulenone 2 (168 mg, 48%), which formed yellow needles from hexane–benzene: mp 162–163 °C dec; mass spectrum, m/e 234 (M^+, 30%), 189 (100); mol wt 234.3; UV, see Tables I and II and Figure 1; IR (KBr) 2200 (w, C≡C), 1635 (s, C=O), 1605 (m, C=C), 1005 cm^{-1} (s, trans HC=CH); ^{1}H NMR (90 MHz, $CDCl_3$, see Table III and Figure 3) τ 2.44 (dd, J = 15, 5 Hz, 1 H, $H^{B'}$), 2.75 (d, J = 11 Hz, 2 H, H^C and $H^{E'}$), 3.19 (dd, J = 16, 5 Hz, 1 H, $H^{C'}$), 3.35 (d, J = 16 Hz, 1 H, H^A), 4.17 (dd, J = 16, 11 Hz, 1 H, H^B), 4.37 (d, J = 15 Hz, 1 H, $H^{A'}$), 4.53 (dd, J = 15, 12 Hz, 1 H, $H^{D'}$), 7.76 (s, 3 H, Me), 7.82 (s, 3 H, Me); ^{1}H NMR (90 MHz, CF_3COOD, determined with CH_2Cl_2 as an internal standard, see Table III) τ 0.29 (dd, J = 15, 6 Hz, 1 H, $H^{B'}$ or $H^{C'}$), 0.89 (d, J = 12 Hz, 2 H, H^C and $H^{E'}$), 1.28 (dd, J = 15, 6 Hz, 1 H, $H^{B'}$ or $H^{C'}$), 1.31 (d, J = 15 Hz, 1 H, H^A), 6.73 (s, 3 H, Me), 6.82 (s, 3 H, Me), 9.92 (dd, J = 15, 12 Hz, 1 H, H^B or $H^{D'}$), 10.10 (d, J = 15 Hz, 1 H, $H^{A'}$), 10.15 (dd, J = 15, 12 Hz, 1 H, H^B or $H^{D'}$).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.38; H, 5.92.

8-Methyl-3,5,7-decatrien-9-yn-2-one (9). An ice-cooled solution of aqueous sodium hydroxide (0.65 N, 1.5 mL) and ethanol (1.5 mL) was added to an ice-cooled stirred solution of dienyne aldehyde 7 (0.60 g, 5 mmol) in acetone (2.7 mL). The solution was stirred for a further 1 h at 0 °C and aqueous sulfuric acid (2 N, 1.6 mL) was then added. The solution was diluted with water and extracted with ether, and the extracts were washed with saturated aqueous sodium bicarbonate. The residue after solvent removal was chromatographed on alumina (Woelm, 100 g). Fractions eluted with 10% ether–pentane on evaporation afforded the ketone 9 (0.62 g, 78%) as orange cubes, mp 64–65 °C, from hexane–ether: UV (Et_2O) λ_{max} 305 (ϵ 18 500), 322 (25 800), 334 (sh, 24 000), 386 nm (sh, 2540); IR (CCl_4) 3280 (m, C≡CH), 2090 (w, C≡C), 1660 (s, C=O), 1595 (s, C=C), 1000 cm^{-1} (s, trans HC=CH); ^{1}H NMR (60 MHz, $CDCl_3$) τ 2.79 (dd, J = 15.5, 11 Hz, 1 H, H^B), 2.92 (dd, J = 14.5, 11.5 Hz, 1 H, H^D), 3.60 (d, J = 11.5 Hz, 1 H, H^E), 3.65 (dd, J = 14.5, 11.5 Hz, 1 H, H^C), 3.84 (d, J = 15.5 Hz, 1 H, H^A), 6.58 (s, 1 H, C≡CH), 7.72 (s, 3 H, Me[a]), 8.00 (s, 3 H, Me[b]). Addition of Eu(fod)$_3$ shift reagent effected complete separation of the overlapping bands at τ 2.79 and 2.92.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.29; H, 7.63.

3,5-Dimethyl-3,5,7,10,12,14-heptadecahexaene-1,16-diyn-9-one (10). Methanolic potassium hydroxide (3.6 N, 2.3 mL) was added to a stirred solution of ketone 9 (0.97 g, 6 mmol) and aldehyde 7 (0.73 g, 6 mmol) in deoxygenated ether (41 mL) at 0 °C. After 1.5 h at 0 °C, acetic acid (2.3 mL) was added, followed by stirring for 15 min and then dilution with water (100 mL). The separated aqueous layer was extracted with benzene and the combined organic extracts were washed with saturated aqueous sodium bicarbonate. The residue after solvent removal was chromatographed on alumina (Merck, 120 g). The initial fractions gave the unchanged ketone 9 (150 mg). Later fractions (30% ether in hexane as eluant) gave the ketone 10 (0.65 g, 41%) as a crystalline liquid. It formed brown plates, mp 123 °C dec, from hexane–benzene: UV (Et_2O) λ_{max} 268 (sh, ϵ 20 500), 279 (23 700), 289 (22 800), 320 (sh, 23 400), 378 nm (54 500); IR ($CHCl_3$) 3290 (m, C≡CH), 2100 (w, C≡C), 1640 (s, C=O), 1605 (s, C=C), 1010 cm^{-1} (s, trans HC=CH); ^{1}H NMR (100 MHz, $CDCl_3$) τ 2.64 (dd, J = 14.5, 11.5 Hz, 2 H, H^D), 2.92 (dd, J = 15.5, 11.5 Hz, 2 H, H^B), 3.57 (d, J = 15.5 Hz, 2 H, H^A), 3.60 (d, J = 11.5 Hz, 2 H, H^E), 3.61 (dd, J = 14.5, 11.5 Hz, 2 H, H^C), 6.59 (s, 2 H, C≡CH), 8.01 (s, 6 H, Me).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.71; H, 6.65.

7,12-Dimethyl-8,10-bisdehydro[17]annulenone (3). A solution of 10 (3.14 g, 12 mmol) in pyridine was added dropwise to a stirred solution of cupric acetate monohydrate (34.5 g) in pyridine (115 mL) during 20 min at 50 °C. The solution was stirred at 55–65 °C for a further 3 h and then cooled. The residue after solvent removal was extracted thoroughly with ether, the solid was removed by filtration, and the filtrate was washed with 3 N hydrochloric acid and then with saturated aqueous sodium bicarbonate. The residue after solvent removal was chromatographed on alumina (Woelm, 300 g). Fractions eluted with 30% ether in pentane on evaporation afforded the annulenone 3 (1.18 g, 38%) as a solid. It formed red needles, mp 207 °C dec, from benzene: mass spectrum, m/e 260 (M^+, 25%), 202 (100); mol wt 260.3; UV, see Tables I and II and Figure 1; IR (KBr) 2200 (w, C≡C), 1610 (s, C=O), 1590 (m, C=C), 990 cm^{-1} (s, trans HC=CH); ^{1}H NMR (100 MHz, $CDCl_3$, see Table III and Figure 1) τ 1.37 (dd, J = 15.5, 11 Hz, 2 H, H^D), 1.40 (dd, J = 16.5, 11 Hz, 2 H, H^B), 3.67 (d, J = 11 Hz, 2 H, H^E), 3.98 (dd, J = 15.5, 11 Hz, 2 H, H^C), 4.20 (d, J = 16.5 Hz, 2 H, H^A), 8.23 (s, 6 H, Me); ^{1}H NMR (90 MHz, CF_3COOD, see Table III) τ −1.68 (dd, J = 16, 11 Hz, 2 H, H^B or H^D), −1.75 (dd, J = 16, 11 Hz, H^B or H^D), 4.09

(16) Hyflo Super-Cel was obtained from Wako Pure Chemicals Co., Ltd.

(d, J = 11 Hz, 2 H, H^E), 4.29 (d, J = 16 Hz, 2 H, H^A), 4.36 (dd, J = 16, 11 Hz, 2 H, H^C), 8.42 (s, 6 H, Me).

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.49; H, 6.24.

3,9-Dimethyl-3,5,7,10,12,14,16-nonadecaheptaene-1,18-diyn-9-one (12). An ethanolic sodium ethoxide solution (12 mL) [from sodium (760 mg) and dry ethanol (100 mL)] was added to a solution of ketone **9** (2.38 g, 15 mmol) in deoxygenated ether (117 mL), and a solution of trienyne aldehyde **11** (2.61 g, 18 mmol) in deoxygenated ether (18 mL) was added dropwise over 1.5 h with stirring at 2–3 °C. After being stirred for a further 4 h at the same temperature, the reaction mixture was quenched by addition of saturated aqueous oxalic acid (3 mL). The solution was poured into water and the mixture was extracted with benzene. The solid was removed by filtration, and the filtrate was washed with saturated aqueous sodium bicarbonate. The residue after solvent removal was chromatographed on alumina (Merck, 110 g). Initial fractions gave unchanged ketone **9** (259 mg). Later fractions, eluted with 50% ether–hexane, afforded ketone **12** (4.20 g, 63%) as a solid, which on crystallization from chloroform–ethanol gave brown microcrystals: mp 250 °C dec; UV (Et_2O) λ_{max} 232 (sh, ϵ 8840), 278 (sh, 15 300), 288 (sh, 17 600), 390 nm (45 500); IR ($CHCl_3$) 3280 (m, C≡CH), 2180 (w, C≡C), 1640 (s, C=O), 1610 (s, C=C), 1005 cm^{-1} (s, trans HC=CH); ^1H NMR (90 MHz, $CDCl_3$) τ 2.43–3.73 (m, 12 H, olefinic H), 6.52 (s, 1 H, C≡CH), 6.55 (s, 1 H, C≡CH), 7.79 (s, 6 H, Me).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.65; H, 6.80.

7,12-Dimethyl-8,10-bisdehydro[19]annulenone (4). A solution of ketone **12** (490 mg, 1.7 mmol) in pyridine and dry ether (3:1, 36 mL) was added dropwise during 2.5 h to a stirred solution of anhydrous cupric acetate (2.1 g) in pyridine and dry ether (3:1, 80 mL) at 45–50 °C (bath). The solution was stirred at 47 °C (bath) for a further 2.5 h and was then cooled. After workup as described for the isolation of **2**, the residue after solvent removal was chromatographed on alumina (Merck, 150 g). The fractions eluted with ether contained the annulenone **4**. The slightly crude **4** was again chromatographed on alumina (Merck, 80 g). Fractions eluted with ether on evaporation afforded the annulenone **4** (25 mg, 5.2%). It formed orange needles, mp 124–125 °C, from hexane–benzene: mass spectrum, m/e 286 (M^+, 66%), 228 (100); mol wt 286.4; UV, see Tables I and II and Figure 1; IR (KBr) 2150 (w, C≡C), 1640 (s, C=O), 1610 (m), 1590 (m, C=C), 980 cm^{-1} (s, trans HC=CH); ^1H NMR (90 MHz, $CDCl_3$, see Table III and Figure 3) τ 2.87–3.22 (m, 5 H, $H^{B'}$ or $H^{C'}$, H^C, H^E, $H^{E'}$, $H^{G'}$), 3.33 (dd, J = 15, 7 Hz, 1 H, $H^{B'}$ or $H^{C'}$), 3.52 (d, J = 15 Hz, 1 H, H^A), 3.80 (d, J = 15 Hz, 1 H, $H^{A'}$), 3.98 (dd, J = 15, 11 Hz, 1 H, H^B or $H^{D'}$), 4.10 (dd, J = 15, 11 Hz, 1 H, H^B or $H^{D'}$), 4.15 (dd, J = 15, 11 Hz, 1 H, H^D or $H^{F'}$), 4.35 (dd, J = 15, 11 Hz, 1 H, H^D or $H^{F'}$), 7.79 (s, 3 H, Me), 7.85 (s, 3 H, Me); ^1H NMR (100 MHz, CF_3COOD, determined with CH_2Cl_2 as an internal standard, see Table III) τ 1.2–1.8 (m, 7 H, H^A, $H^{B'}$, H^C, $H^{C'}$, H^E, $H^{E'}$, $H^{G'}$), 6.96 (s, 3 H, Me), 7.07 (s, 3 H, Me), 8.4–9.1 (m, 5 H, $H^{A'}$, H^B, $H^{B'}$, H^D, $H^{D'}$, $H^{F'}$). This spectrum changed on standing, suggesting the occurrence of a transformation to a different compound.

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.86; H, 6.12.

10-Methyl-3,5,7,9-dodecatetraen-11-yn-2-one (13). An ice-cooled solution of aqueous sodium hydroxide (0.65 N, 3 mL) and ethanol (3 mL) was added to an ice-cooled solution of aldehyde **11** (1.33 g, 9.1 mmol) in acetone (5.4 mL). The solution was stirred for a further 1 h at 0 °C, and aqueous sulfuric acid (2 N, 1.4 mL) was then added. After workup as described for the isolation of **9**, the residue after solvent removal was chromatographed on alumina (Woelm, 100 g). Fractions eluted with 20% ether–pentane afforded the ketone **13** (0.92 g, 54%) as a crystalline liquid. It formed brown needles, mp 84–85 °C, from hexane–ether: UV (Et_2O) λ_{max} 246 (sh, ϵ 6760), 254 (8520), 333 (sh, 53 300), 349 (76 400), 365 nm (70 000); IR (KBr) 3300 (m, C≡CH), 2100 (w, C≡C), 1675 (s, C=O), 1600 (s, C=C), 1005 cm^{-1} (s, trans HC=CH); ^1H NMR (60 MHz, $CDCl_3$) τ 2.70–4.01 (m, 7 H, olefinic H), 6.61 (s, 1 H, C≡CH), 7.72 (s, 1 H, Me^a), 8.02 (s, 3 H, Me^b).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.94; H, 7.58.

3,9-Dimethyl-3,5,7,9,12,14,16,18-heneicosaoctaene-1,20-diyn-11-one (14). An ethanolic sodium ethoxide solution (1.5 mL) [from sodium (380 mg) and dry ethanol (50 mL)] was added to a solution of ketone **13** (437 mg, 2.4 mmol) in deoxygenated ether (19 mL), and a solution of trienyne aldehyde **11** (344 mg, 2.4 mmol) in deoxygenated ether (5 mL) was added dropwise during 25 min with stirring at 5–6 °C. After being stirred for a further 3 h at this temperature, the reaction mixture was quenched by addition of saturated aqueous oxalic acid (5 mL). After workup as described for the isolation of **12**, the residue after solvent removal was chromatographed on alumina (Merck, 100 g). Initial fractions gave unchanged ketone **13** (151 mg). Later fractions, eluted with 60% ether–hexane, on evaporation afforded the ketone **14** (229 mg, 31%) as a solid. Recrystallization from hexane–benzene gave brown microcrystals: mp 94 °C dec; mass spectrum, m/e 314 (M^+, 31%), 145 (100); mol wt 314.4; UV (THF) λ_{max} 227 (sh, ϵ 9560), 268 (sh, 11 600), 282 (sh, 16 000), 304 (sh, 22 000), 323 (22 800), 403 nm (56 600); IR (KBr) 3300 (m, C≡CH), 2100 (w, C≡C), 1650 (m, C=O), 1610 (s, C=C), 1000 cm^{-1} (s, trans HC=CH); ^1H NMR (100 MHz, $CDCl_3$) τ 2.53–3.78 (m, 14 H, olefinic H), 6.61 (s, 2 H, C≡CH), 8.02 (s, 6 H, Me).

Satisfactory microanalytical figures could not be obtained, presumably due to the instability of **14**.

9,14-Dimethyl-10,12-bisdehydro[21]annulenone (5). A solution of ketone **14** (569 mg, 1.81 mmol) in pyridine and dry ether (3:1, 84 mL) was added dropwise during 3 h to a stirred solution of anhydrous cupric acetate (2.3 g) in pyridine and dry ether (3:1, 84 mL) at 45–50 °C (bath). The solution was stirred at the same temperature for a further 2.5 h and was then cooled. After workup as described for the isolation of **2**, the residue was chromatographed on alumina (Merck, 150 g). Elution with ether and evaporation yielded crude **5**, which was again chromatographed on alumina (Merck, 90 g). The fractions, eluted with 90% ether–petroleum ether (bp 40–65), on evaporation afforded **5** (46 mg, 8.1%) as crystals. Recrystallization from hexane–benzene gave red needles: mp 159–160 °C; mass spectrum, m/e 312 (M^+, 66%), 253 (100); mol wt 310.4; UV, see Tables I and II and Figure 1; IR (KBr) 2150 (m, C≡C), 1640 (m, C=O), 1615 (s), 1590 (s, C=C), 1005 cm^{-1} (s, trans HC=CH); ^1H NMR (100 MHz, $CDCl_3$, see Table III and Figure 4) τ 1.94 (dd, J = 16, 11 Hz, 4 H, H^D, H^F), 2.36 (dd, J = 16, 11 Hz, 2 H, H^B), 3.63 (d, J = 11 Hz, 2 H, H^G), 3.84 (dd, J = 16, 11 Hz, 2 H, H^C, or H^E), 3.88 (dd, J = 16, 11 Hz, 2 H, H^C or H^E), 4.16 (d, J = 16 Hz, 2 H, H^A), 8.17 (s, 6 H, Me); ^1H NMR (100 MHz, CF_3COOD, see Table III) τ −2.22 (dd, J = 16, 11 Hz, 2 H, H^D or H^F), −2.10 (dd, J = 16, 11 Hz, 2 H, H^D or H^F), −1.62 (dd, J = 16, 11 Hz, 2 H, H^B), 4.28–4.80 (m, 8 H, H^A, H^C, H^E, H^G), 8.52 (s, 6 H, Me).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.16; H, 6.18.

Acknowledgment. We thank Miss Yukiko Makagawa, Toyama University, for her experimental help as well as the Royal Society for financial support.

Registry No. **1**, 55338-03-9; **2**, 74231-35-9; **3**, 74231-36-0; **4**, 74231-37-1; **5**, 74231-38-2; **6**, 58964-85-5; **7**, 55304-70-6; **8**, 74231-39-3; **9**, 74231-40-6; **10**, 74231-41-7; **11**, 68520-89-8; **12**, 74231-42-8; **13**, 74231-43-9; **14**, 74244-54-5; **15**, 61966-95-8.